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Tracking Energy Relaxation Within Plasmonic Metal Oxide
Nanocrystals

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## Abstract

Plasmonic noble metal nanocrystals (NCs) have received a large amount of research interest due to their ability to harvest light and direct it into a small region of space. However, the intrinsic high free carrier concentration of noble metal NCs makes it challenging to achieve plasmonic structures with strong absorption profiles in the near-infrared spectral range, which is relevant for telecommunications and photonics applications. As an alternative to noble metal structures, transition metal oxide NCs possess low intrinsic free carrier concentrations, but can be sufficiently doped such that they display broad plasmon resonances in the near- and mid-infrared spectral regions. Moreover, the free carrier concentrations of metal oxide NCs can be dynamically modified via electrical, chemical, or photonic means, making these promising materials for the design of smart windows with electrically tunable transmission properties and fast photonic gates and switches. However, developing applications based on plasmonic metal oxide NCs requires understanding how the internal structure of these materials impacts both their steady-state absorption properties and how these properties change when a NC is perturbed from equilibrium. In this report, we have used transient absorption spectroscopy to examine how photoexcitation modifies the optical properties of two metal oxide systems, Sn-doped indium oxide (ITO) NCs and oxygen-vacancy doped tungsten oxide ($WO_{3-x}$) NCs. Plasmonic excitation of either material generates hot electrons on a sub-picosecond timescale that later cool by releasing their energy to lattice phonons. Both of these processes alter the center frequency and linewidth of a NC's plasmon resonance, but the magnitude of these changes depend on the NC's size, crystallographic structure, and the spatial location of dopants within it. We have also investigated how bandgap photoexcitation can be used to manipulate the plasmon resonance of $WO_{3-x}$ NCs. Adding additional charge carriers into the conduction band of these NCs induces a hypsochromic shift of their plasmon resonance that dissipates on picosecond timescales once the exciting field is removed, making these materials interesting candidates for fast photoswitches and photonic gates.

## Overview of Research Accomplishments

- Plasmonic nanocrystals (NCs) of tin-doped indium oxide (ITO) were investigated using transient absorption spectroscopy. While indium oxide is a semiconductor, the inclusion of n-type Sn dopants moves the NCs' fermi energy into their conduction band, rendering them metallic. As such, ITO NCs display plasmonic absorption features in the near-infrared region. Photoexcitation of the plasmon band results in photobleaching of this entire resonance that nearly recovers within our experimental time-resolution ~100 fs. Residual bleaching of the band and weak induced absorption features that persist over nanoseconds are also observed and can be ascribed to phonon excitation following plasmon relaxation. These spectral features can be described by a two-temperature model that maps spectral changes onto time-dependent changes in the electron gas and phonon temperatures of the NCs following photoexcitation. Interestingly, we observe differing phonon relaxation dynamics for ITO NCs depending on the spatial placement of dopants within them. The rapid photobleach recovery we observe at short delays indicates that ITO NCs may be ideal materials for the design of fast photonic gates and switches in the near-infrared spectral range. A manuscript describing these results is in preparation for submission to an emerging investigators issue of *J. Mater. Chem. C* in January 2017.

- Oxygen-vacancy and cesium-doped tungsten oxide ($WO_{3-x}$) NCs were also investigated to vet the spectral model described above. The free carrier concentrations of these NCs are higher than that of ITO NCs, which allows their plasmon resonances to extend into the visible spectral range. While the relaxation behavior of these materials is qualitatively similar to that of ITO NCs, we observe in small diameter particles (~5 nm) a recurrence of the photobleach on timescales of ~100 ps that was not anticipated. We attribute this recurrence to thermal expansion of the $WO_{3-x}$ lattice, which decreases their free carrier concentration and leads to a shift of their plasmon absorption resonance.

- We have used transient absorption to investigate changes in the optical properties of oxygen-vacancy doped $WO_{3-x}$ NCs following excitation of their bandgap in the ultraviolet region. Promotion of carriers from the valence to conduction band of $WO_{3-x}$ NCs is expected to alter their free carrier concentration and shift their plasmon resonance to higher energy as a result. While we do observe this expected shift, we find that its strength is strongly dependent on the structure of the $WO_{3-x}$ NC. 10 nm diameter NCs with a cubic crystal structure display larger spectral shifts than samples composed of 30 nm diameter $WO_{3-x}$ NCs with a hexagonal crystal structure. Currently, it is unclear if the difference in crystal structure or average particle size of these samples leads to this behavior. We are continuing to work in this area to identify the structural properties of $WO_{3-x}$ NCs that promote spectral shifts upon bandgap excitation. Such information can aid the design of photonic switches based on these materials.

- We have made key upgrades to our laboratory infrastructure that have been critical to the success of this project. Specifically, we have extended the probing range of our transient absorption spectrometer into the near-infrared through the incorporation of an InGaAs photodiode array with read speeds of up to 9.1 kHz. We have also incorporated an excitation source (TOPAS-Prime optical parametric amplifier) capable of producing ~100 fs excitation pulses that are tunable from ~1.1 μm to 2.6 μm. Both infrastructure improvements are required for the femtosecond stimulated Raman (FSRS) experiments outlined under *Specific Aim 1* of the proposal. These experiments were delayed due to unexpected difficulty in sample preparation, but are now slated to start in earnest this Spring semester.

- We have used transient absorption measurements and theoretical calculations to investigate how the exciton delocalizing ligand, phenyldithiolcarbamate (PTC), alters charge carrier relaxation pathways within CdSe NCs. Interestingly, we found that PTC's ability to accept charge from CdSe NCs is highly contingent on the manner with which it binds to the NC surface. A summary describing this work was published in the *Journal of Physical Chemistry C* in November 2016. While this work is outside the scope of our original proposal, its completion proved beneficial to this project as it allowed us to compose a general procedure for achieving NC ligand exchange, a necessary step for the FSRS experiments described in *Specific Aim 1* of this proposal.

## Project Goals & Research Findings

### Overview & Project Goals:

While many common transition metal oxides are wide-gap semiconductors, these materials can be rendered metallic through the inclusion of either n- or p-type dopants. Materials such as $In_2O_3$, $WO_3$, and $Cu_2S$ can each be sufficiently doped to the point that their Fermi energy resides within their conduction or valence band, enabling them to display plasmonic absorption resonances in the near- and mid-infrared spectral ranges. Moreover, by modulating the free carrier concentrations of these materials through optical, electrical, chemical or thermal means, the absorption amplitude and spectral position of these plasmon resonances can be dynamically altered. As such, doped transition metal oxides provide a versatile platform for the design of near-infrared photonic gates, chemical sensors, and smart windows whose transmission properties can be altered through the application of voltage or heat.

Nanocrystals (NCs) of doped transition metal oxides offer an appealing design platform for these applications. Due to their small size, only a small number of free charge carriers need to be introduced to a metal oxide NC to alter its free carrier concentration and shift its optical properties. Likewise, their high surface-to-volume ratio can facilitate rapid optical switching by ensuring that charge carriers do not need to travel over large distances to exit or enter an individual NC. However, designing composite materials that utilize transition metal oxide NCs for optoelectronic applications requires understanding how the optical properties of these particles change when they are perturbed from equilibrium. In particular, the linewidth and spectral position of the plasmon resonances of transition metal oxide NCs have each been shown to strongly depend not only on their dopant concentration, but also on their size, crystal structure, and the spatial location of dopants within them. *A priori*, it is not clear the extent to which the plasmon resonances of NCs with differing internal structures can be modulated by external stimuli such as temperature, potential bias, and light. To directly address this lack of information, our goals in this project were to: (1) determine the degree to which the optical properties of metal oxide NCs comprised of Sn-doped $In_2O_3$ (ITO) can be altered by photoexcitation; (2) map how these changes differ depending on the size and spatial placement of dopants within the NCs; and (3) identify the relaxation processes that dissipate the energy of photons absorbed by the NCs to their environment.

As of the time of this report, we have used femtosecond transient absorption measurements to address the three goals listed above. In these measurements, a short near-infrared or optical pulse is used to photoexcite a NC sample. Changes in the sample's absorption spectrum are subsequently read out by a spectrally-broad, time-delayed probe pulse. Below, we provide a description of the key results and accomplishments of this project.

### Changes in the Optical Properties of ITO Nanocrystals Induced by Plasmon Excitation

Prior work examining noble metal nanostructures has shown that plasmonic excitations dissipate their energy on femtosecond timescales, creating hot charge carriers. Over longer timescales of hundreds of femtoseconds to picoseconds, these hot carriers release their energy via electron-phonon coupling, heating the nanostructure's crystal lattice. For a plasmonic transition metal oxide NC, these two processes should lead to distinct changes in the NC's plasmon absorption lineshape. Specifically, the generation of hot electrons within a NC is expected to lower the high frequency dielectric constant of the NC, leading to a decrease in the peak position of its plasmon absorption lineshape. By that same token, heating the phonon bath of a NC will raise the rate with which plasmon excitations are damped by internal NC vibrations, causing the NC's plasmon lineshape to broaden. While both of these optical effects are expected for many plasmonic structures in addition to plasmonic metal oxide NCs, a general understanding of how the magnitude of these effects depends on the structure and composition of a metal oxide NC is not clear. For example, dispersing Sn dopants uniformly throughout ITO NCs vs in a thin shell at their surfaces has been shown to lead to distinctly different plasmon absorption lineshapes (Figure 1A) due to changes in surface

plasmon damping. Similarly, these differing placements of dopants could lead to spatial variations in electron-phonon coupling within ITO NCs, resulting in differences among structurally distinct NCs in both the timescales for hot electron dissipation and the magnitude of the lattice temperature changes that occur upon hot electron cooling.

To determine the timescales for kinetic processes tied to plasmon relaxation within ITO NCs and characterize how these timescales depend on NC internal structure, we have used transient absorption measurements that directly excite the surface plasmon resonances of ITO NCs with a femtosecond near-infrared pump pulse and then subsequently read out changes in the plasmon lineshape with a spectrally broad, time-delayed probe pulse (Figure 1B).



**Figure 1:** (A) Absorption spectra displaying the near-infrared plasmon resonance of ITO NCs containing Sn dopants that are either uniformly dispersed throughout the particle or preferentially segregated near their surface. (B) Photoexcitation of the plasmon resonance leads to the creation of a hot electron distribution that relaxes through electron-phonon coupling. (C) Experimental transient absorption spectra of homogeneously (left) and surface (middle) doped ITO NCs as well as a fit from a spectroscopic model (right) to the surface doped data. Note, the time origin of the experimental data has been adjusted by 300 fs for plotting purposes.

Representative transient absorption kinetic traces for homogeneously Sn-doped and selectively surface doped ITO NCs suspended in tetrachloroethane are shown in Figure 1C. Relaxation of the excited surface plasmon to generate hot carriers occurs on a timescale that is shorter than the time-resolution of our transient absorption spectrometer (~100 fs). As such, for both NC samples we observe a near instantaneous growth of a broad photobleaching signal that can be attributed to a shift of the NCs' plasmon resonance to lower energy due to hot electron formation. Relaxation of this hot electron population occurs over the course of ~250 fs, leading to a rapid recovery of the observed photobleaching signal. Further examination of the transient absorption spectra over picosecond time delays reveals the existence of a weak, but persistent negative signal that can more easily be seen in spectra of surface-doped particles. We attribute this small, but clearly noticeable signal to broadening of the plasmon lineshape due to warming of the ITO NC lattice stemming from the coupling of hot electrons to lattice phonon modes.

To quantitatively describe the transient changes we observe upon NC plasmon excitation, we have developed a spectroscopic model that adequately reproduces our transient absorption spectra. A fit produced by this model to transient spectra measured for surface-doped ITO NCs is shown in Figure 1C. Note that differences in appearance between the model and experimental spectra largely result from differing plot ranges and a small temporal offset applied to the experimental data. Overall, our spectral model captures much of the behavior that we observe in the transient spectra and allows us to estimate the amount of heating of the ITO NCs that results from plasmon excitation. Interestingly, we find that the degree to which ITO NCs are heated by hot electron relaxation is only a small fraction of the amount of heating that occurs in noble metal-based structures as a result of plasmon excitation. While this is in part to be expected based on the lower energy of the plasmon resonance of ITO NCs, the reduced free carrier concentration of these NCs with respect to noble metal-based systems also likely plays a role in this reduced temperature as the change in photon energy alone is insufficient to fully explain the spectral changes that we observe.
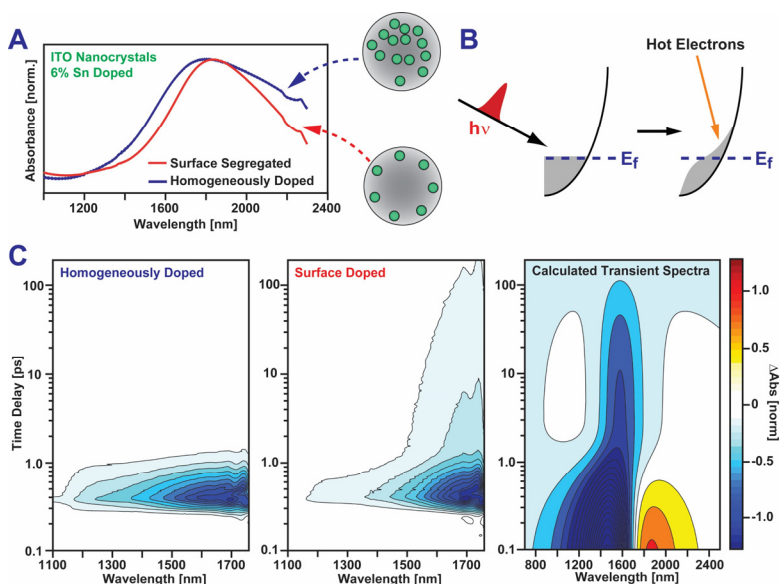
Although the dynamics that we observe are largely similar for surface-doped and homogeneously-doped ITO NC samples, a notable difference between these two data sets is that surface-doped NCs seem to show a larger amplitude signal over picosecond time delays, suggesting that plasmon excitation causes the lattice of these NCs to heat up more than that of uniformly-doped NCs. A potential explanation for these results is that energy transfer between hot electrons and lattice phonons preferentially occurs at dopant sites. Then, over the ultrafast (picosecond) timescales we probe, surface dopant sites would be expected to heat up more due to the smaller density of NC atoms surrounding these sites. This reduced density means that NC surface atoms will have access to a smaller number of phonon states they can transfer energy to, creating an energy transfer bottleneck that can slow the dispersal of energy away from these sites. We are currently in the process of composing a manuscript describing these results that will be submitted to *J. Mater. Chem. C* in January for consideration for inclusion in a special young investigators issue being produced by the journal.

### *Plasmon Lineshape Modification due to NC Thermal Expansion*

In addition to our studies of ITO NCs, we have carried out transient absorption measurements of tungsten oxide NCs ($WO_{3-x}$). These materials possess oxygen vacancies that render them n-type and contain higher free carrier populations than ITO NCs, which shifts the $WO_{3-x}$ plasmon resonance closer to the visible spectral range. From an applications point-of-view, the location of the $WO_{3-x}$ plasmon resonance at the high-energy edge of the near-infrared spectral range creates the potential to use $WO_{3-x}$ in the construction of photochromic filters that can be switched between transparent or opaque states at visible wavelengths. Interestingly, this material can be further doped through the inclusion of cesium atoms, which also changes the crystal structure of the NCs from cubic to hexagonal. The asymmetric crystal structure of hexagonal $WO_{3-x}$ NCs leads to the appearance of two distinct plasmon bands, that can be attributed to longitudinal and transverse plasmon modes (Figure 2, top).



We have used transient absorption to monitor spectral changes in the absorption profile of both cubic and hexagonal $WO_{3-x}$ NCs following plasmon excitation and found that their relaxation behavior is similar to that of ITO NCs. Upon photoexcitation, a bathochromic shift of the NCs' plasmon resonance is observed due to hot electron formation. As these electrons cool and heat the NC lattice, spectral broadening of the NC's plasmon resonance occurs. A representative dataset illustrating this behavior for hexagonal $WO_{3-x}$ NCs is shown in Figure 4 below. As expected on the basis of their higher carrier concentration with respect to ITO NCs, $WO_{3-x}$ NCs appear to thermalize to a higher lattice temperature than ITO NCs. This observation will be included in a manuscript currently in preparation for submission to *J. Mater. Chem. C* in January.

Interestingly, upon examining how the kinetics of plasmon relaxation change as the size of the $WO_{3-x}$ NC is altered, we observed an unexpected result for NCs with diameters of 5 nm or less. Following electron-phonon equilibration on a timescale of <1 ps, we see a slow growth of plasmon photobleaching signal that is not predicted by our spectral model (Figure 2, bottom). The growth of this signal results from shifting of the NCs' plasmon resonance over 100s of picoseconds following excitation. Our current hypothesis to explain this observation is that it results
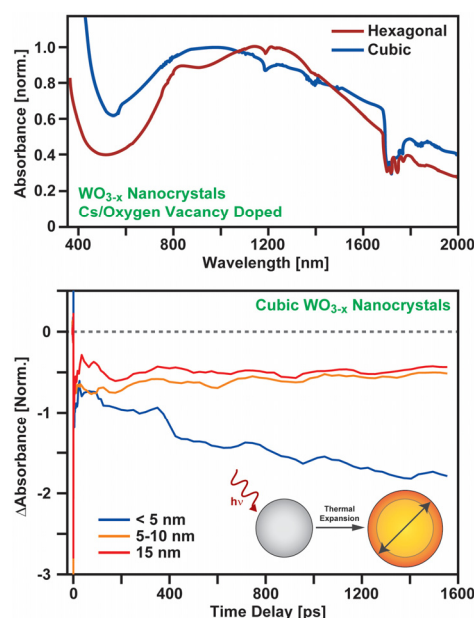
**Figure 2:** (Top) Absorption spectra of cubic and hexagonal $WO_{3-x}$ NCs suspended in hexane. (Bottom) Transient absorption kinetics of cubic NCs of different diameters measured at a probe wavelength of 1200 nm. The growth of photobleaching signal over 100s of picoseconds for the smallest diameter particles is attributable to thermal expansion of the NC lattice.

from thermal expansion of the NCs, which can decrease the free carrier concentration of a NC by increasing its volume, and hence lead to a shift of its plasmon resonance. As both small and large NCs are expected to experience similar changes in lattice temperature upon plasmon relaxation, we expect both large and small NCs to display similar changes in the size of their unit cells. As such, both small and large NCs will undergo similar absolute changes in their diameter, which will lead to a larger percentage change in the volume of smaller NCs due to their larger surface-to-volume ratio. This change in volume can lead to the additional spectral shifting that we observe. While such thermal expansion-induced shifts have been seen for the plasmon resonances of metallic nanostructures, this work is to our knowledge the first report of such shifts in doped transition metal oxide NCs. In principle, this effect could be used to read out the absolute temperature of small $WO_{3-x}$ NCs, thereby allowing these materials to be used as nanoscopic temperature probes with sub-nanosecond response times.

### *Bandgap Excitation of Transition Metal Oxide NCs can Shift their Plasmon Resonances*

We have also performed transient absorption measurements that utilized an ultraviolet excitation pulse to promote charge carriers from the valence band of $WO_{3-x}$ NCs to their conduction band. Such excitation can increase the concentration of free charge carriers within the NCs, leading to a hypsochromic shift of their plasmon resonance (Figure 3, top). Two different samples of oxygen vacancy doped $WO_{3-x}$ NCs were investigated, the first consisting of NCs with a cubic structure while the second was comprised of hexagonally shaped NCs that contained additional cesium-dopants. Absorption spectra of both NC samples suspended in hexane are displayed in the lower portion of Figure 3 alongside representative transient absorption spectra of these samples measured for time delays averaged between 150 fs and 2 ps. For both samples, the transient absorption spectrum is comprised of a negative signal that overlaps with their steady-state plasmon absorption resonance and a positive, photo-induced absorption signal that appears to the high-energy side of this resonance. Taken together, these spectral signatures suggest that bandgap excitation leads to a shifting of the plasmon resonance of each NC to higher energy.

Notably, the magnitude of the shift observed for each NC sample differs, even though both sets of experiments produce similar changes in the free carrier density of each sample. This is not unexpected as each sample is comprised of NCs with different average particle sizes. While the cubic NC sample contains crystals with an average diameter of 10 nm, the hexagonal sample consists of NCs with an average diameter of 30 nm. Thus, we would expect for the same level of photoexcitation, a larger proportional change in the carrier concentration of the cubic NC sample, leading to a larger hypsochromic shift of the NC's plasmon absorption resonance. The data shown in Figure 3 suggests this prediction holds true.



**Figure 3:** (Top) Ultraviolet photoexcitation of a doped metal oxide NC increases the number of free carriers in the NC's conduction band, causing the NC's plasmon resonace to shift to higher energy. (Bottom) Absorption spectra of cubic and hexagonal $WO_{3-x}$ NCs plotted alongside transient absorption spectra measured between 0.15 – 2 ps after photoexcitation at 400 nm. For both samples, a distinct photoinduced absorption can be observed on the high frequency side of the plasmon resonance.

However, while this simplistic explanation of our observed results is appealing, the difference in crystal structure between these two samples does complicate the interpretation of our results. Specifically, the plasmon lineshape of hexagonal $WO_{3-x}$ NCs markedly differs from that of cubic NCs due to their asymmetric structure, which leads to the appearance of both longitudinal and transverse plasmon absorption
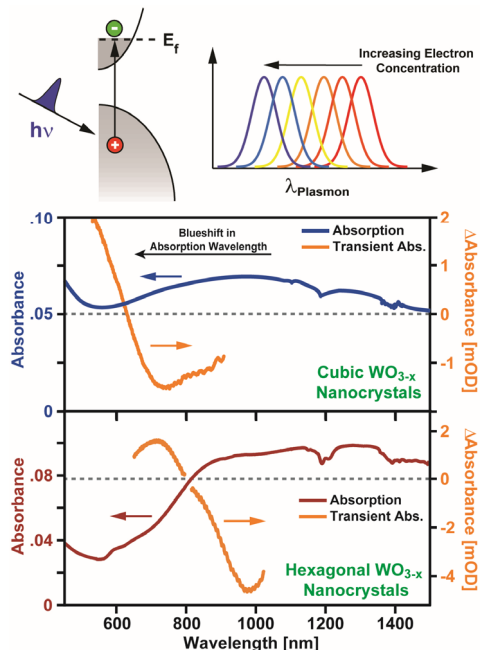
resonances. How each of these resonances shift following bandgap excitation is unclear and interference between spectral changes tied to these two modes could potentially lead to the smaller hypsochromic shift that we observe for hexagonal NCs with respect to cubic NCs. Experiments are currently ongoing that aim to repeat these measurements for a series of cubic and hexagonal NCs of similar size to separately identify how NC size and crystal structure each impact the spectral shifting that we observe.

Despite the differences that we observe in the magnitude of the hypsochromic shifts for cubic and hexagonal $WO_{3-x}$ NCs, we find that these changes relax rapidly, within a few picoseconds following photoexcitation. This result suggests that bandgap excitation of $WO_{3-x}$ NCs can be used to dynamically alter their absorption spectrum, enabling them to be used for photonic gates that shift color only when exposed to ultraviolet radiation. As such these materials may be of potential utility for switches in photonic circuits, dynamic UV and visible protective coatings, and electrochromic windows among other applications.

### *Construction of a Near-Infrared Transient Absorption Spectrometer*

Each of the transient absorption experiments described above make use of either near-infrared excitation or probe pulses. At the outset of this project, resources needed for the for the construction of a near-infrared transient absorption spectrometer within the PI's lab were available, but these items had yet to be assembled into a fully functioning instrument. During the first three months of the project, software and timing circuits for the operation of a 512-pixel InGaAs array detector (Hamamatsu G11620-512) were developed that allows the reading of the array to be synchronized with the firing of a Ti:sapphire amplifier used for transient absorption experiments, which operates at a 3 kHz repetition rate. By detecting a NIR spectrum for every laser shot, this array maximizes the duty cycle of our system and increases its signal-to-noise ratio by allowing for shot-to-shot differencing of transient absorption signals and the use of statistical algorithms to reject spurious data points. An optical parametric amplifier (Light Conversion, TOPAS-Prime) capable of producing excitation pulses tunable from ~1100 – 2400 nm was also integrated into our transient absorption instrument during the initial three months of the project.

Figure 4 displays a representative transient absorption dataset measured for cesium-doped hexagonal $WO_{3-x}$ NCs using these excitation and detection sources. This data set contains spectra measured using both the InGaAs detector described above and a Si CCD camera (Princeton Instruments, PyLoN 100BR) that were combined using an in-house Matlab algorithm. Interestingly, this data displays an initial photobleach of the NCs' plasmon resonance between 1400 - 1500 nm



**Figure 4:** Transient absorption spectra of $WO_{3-x}$ NCs following photoexcitation of their plasmon resonance at 800 nm.

that recovers on a sub-picosecond timescale, but then regrows over the course of a few picoseconds. This back-and-forth behavior is attributable to an initial bathochromic shift of the $WO_{3-x}$ plasmon resonance due to the formation of hot electrons followed by subsequent broadening of the plasmon resonance from the excitation of lattice phonons by hot electrons.
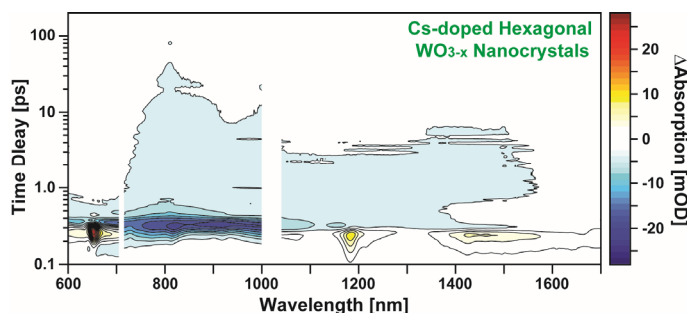
### *Characterizing how Exciton Delocalizing Ligands Impact Carrier Relaxation Dynamics in CdSe NCs*

In addition to our work on plasmonic transition metal oxide NCs, we have investigated how exciton delocalizing ligands (EDLs) influence charge carrier relaxation dynamics in quantum confined CdSe NCs. Typically, the surfaces of CdSe NCs are terminated with long-chain aliphatic ligands that are introduced during synthesis to halt their growth and impart solubility in organic solvents. However, for applications that require the extraction of charge from NCs, such as photocatalysis and solar energy conversion, these long-chain ligands create an insulating barrier that can hinder device performance. In contrast, EDLs are

ligands whose valence orbitals can strongly mix with the band edge states of the NC to which they are bound, creating hybrid states near the edge of the valence and conduction band that extend throughout the NC and its ligand shell. For optoelectronics and photocatalytic applications, EDLs are particularly appealing as they may facilitate charge extraction from NCs.

In our work, we have investigated how the EDL phenyldithiol carbamate (PTC) alters rates for intraband carrier cooling, charge carrier trapping, and charge recombination in quantum confined CdSe NCs. Specifically, we were interested in assessing if PTC can aid the extraction of hot holes from CdSe NCs by making these energized charge carriers spatially accessible before they cool. Treating oleic acid-capped CdSe NCs with a large excess of PTC results in a bathochromic shift of the NCs' the first exciton band of tens to a few hundred meV depending on NC size. These shifts can largely be attributed to electronic coupling between the HOMO level of surface-bound PTC ligands and states contained within the NC valence band. Such coupling results in the formation of hybrid band edge val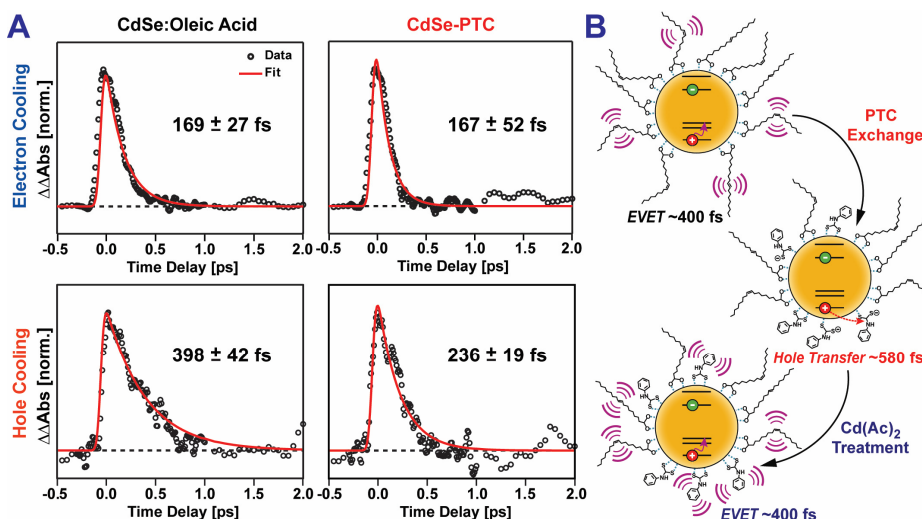ence orbitals that extend over both the NC core and the PTC molecules contained within its ligand shell. However, this strong NC-ligand coupling could also speed intraband cooling of charge carriers via energy transfer to the vibrational modes of surface-bound PTC molecules, reducing the potential to use PTC for hot carrier extraction.



**Figure 5:** (A) Transient absorption kinetics highlighting intraband hole and electron relaxation of CdSe NCs coated with oleic acid and treated with PTC. (B) On the basis of changes that we observe in the intraband hole relaxation rate of CdSe NCs with different surface functionalizations, we conclude that PTC treatment produces at least two distinct surface-bound species, of which one can extract photoexcited holes on a sub-picosecond timescale. Subsequent treatment of CdSe NCs with Cd(Ac)$_2$ removes this species, allowing holes to undergo interband relaxation by transferring energy to vibrational modes of surface bound ligands (electronic to vibrational energy transfer: EVET).

Figure 5A shows kinetics traces obtained using transient absorption spectroscopy that describe the population of hot electrons and hot holes following photoexcitation of oleic acid capped CdSe NCs and CdSe NCs that have been treated with PTC. For specific details regarding the extraction of this information from transient absorption data, we direct interested readers to a recent publication from our group, M. S. Azzaro, M. C. Babin, S. K. Stauffer, G. Henkelman, & S. T. Roberts *J. Phys. Chem. C.* **DOI:** 10.1021/acs.jpcc.6b08178, (2016), which acknowledges AFOSR support. The traces shown in the top of Figure 5A show that PTC has little impact on the cooling rate of hot electrons, which is not unexpected as PTC has only a minor influence on the structure of the conduction band of CdSe NCs. In contrast, PTC treatment appears to accelerate the rate of hole cooling by nearly a factor of two. In addition to this result, we found that the acceleration of the hole cooling rate can be undone by treating PTC-functionalized NCs with cadmium(II) acetate (Cd(Ac)$_2$). Cd$^{2+}$ ions are known to coordinate PTC molecules, forming them into aggregates that fall out of solution. Interestingly however, we saw that treatment with Cd(Ac)$_2$ does not remove the bathochromic shift indicative of PTC molecules bound to the surface of CdSe, implying that Cd$^{2+}$ ions do not remove all PTC molecules bound to CdSe NC surfaces.

These observations led us to hypothesize that at least two distinct populations of PTC molecules exist on CdSe NC surfaces, one that causes rapid hole cooling and can be removed by Cd$^{2+}$ ions, and another that facilitates hole delocalization. These conclusions are supported by DFT calculations and FT-IR spectra of

PTC and Cd(Ac)$_2$ treated CdSe NC films, which show evidence suggesting that PTC can attach to CdSe NC surfaces via a variety of different binding geometries. Moreover, these experiments and calculations suggest that the rapid hole relaxation that we observe for PTC-treated samples results not from intraband cooling, but rather from hole transfer to loosely bound PTC molecules that can be removed by Cd$^{2+}$.

Our conclusions from this work are that PTC molecules do not lead to an acceleration of the intraband hole cooling rate of CdSe NCs and may provide a platform for developing NC-based applications that make use of hot hole transfer. Our results also highlight that the electronic structure of NCs functionalized with EDLs can be strongly dependent on the manner in which the EDLs bind to the NC surface. While this work is outside the scope of the goals outlined in our initial proposal focused on transition metal oxide NCs, we believe that the lessons learned from it regarding NC ligand exchange and surface functionalization are critical to achieving photocatalytic and light harvesting applications that utilize transition metal oxide NCs to transfer energy to surface-bound or adsorbed ligands. More specifically, this work will inform efforts in the PI's lab to functionalize ITO NCs with reporter molecules designed to measure the distance over which plasmonic excitations can transfer energy to surface bound molecules. Experiments to measure this distance using femtosecond stimulated Raman spectroscopy (FSRS) are slated to commence in Spring 2017.

## Publications Produced to Date that Acknowledge this Award

1. M. S. Azzaro, M. C. Babin, S. K. Stauffer, G. Henkelman, & S. T. Roberts, "Can exciton-delocalizing ligands facilitate hot hole transfer from semiconductor nanocrystals?" *J. Phys. Chem. C*. **DOI:** 10.1021/acs.jpcc.6b08178, (2016).

## Presentations Given (or to be Given) as a Result of this Award

1. S. T. Roberts, "How does Energy Migrate in Excitonic Systems?" *To be given* at Temple University, Physical Chemistry Seminar, Philadelphia, PA, April 2017. (Oral Presentation)

2. S. T. Roberts, "Extracting Energy from Excitonic Systems" *To be given* at the 253$^{rd}$ American Chemical Society Meeting, San Francisco, CA, March 2017. (Oral Presentation)

3. M. A. Blemker, M. S. Azzaro, R. W. Johns, D. J. Milliron, & S. T. Roberts, "Quantifying Energy Transfer from Transparent Conductive Oxide Nanocrystals' Localized Surface Plasmons to Surface-bound Ligands" Colloidal Semiconductor Nanocrystals Gordon Research Conference, Mount Snow, VT, August 2016. (Poster Presentation)

4. M. S. Azzaro, M. C. Babin, & S. T. Roberts, "Can Exciton-delocalizing Ligands Facilitate Hot Hole Transfer in Semiconductor Nanocrystals?" Colloidal Semiconductor Nanocrystals Gordon Research Conference, Mount Snow, VT, August 2016. (Poster Presentation)

5. M. S. Azzaro, M. C. Babin, & S. T. Roberts, "The Impact of Dithiocarbamate Ligands on the Electronic Structure of CdSe Nanocrystals Viewed by State-Resolved Transient Absorption Spectroscopy" Southwest Ultrafast Conference, Austin, TX, June 2016. (Poster Presentation)

6. M. A. Blemker, M. S. Azzaro, R. W. Johns, D. J. Milliron, & S. T. Roberts, "Quantifying Energy Transfer in Transparent Conductive Oxide Nanocrystals", Southwest Ultrafast Conference, Austin, TX, June 2016. (Poster Presentation)

7. M. S. Azzaro, M. A. Blemker, M. C. Babin, R. W. Johns, D. J. Milliron, & S. T. Roberts, "Tracking Ultrafast Dynamics in Semiconductor Nanocrystals" AFOSR Molecular Dynamics and Theoretical Chemistry Program Review, Arlington, VA, May 2016. (Poster Presentation)

# AFOSR Deliverables Submission Survey

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Tracking Energy Relaxation within Plasmonic Metal Oxide Nanocrystals

**Grant/Contract Number**
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FA9550-15-1-0344

**Principal Investigator Name**
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Sean T. Roberts

**Program Officer**
**The AFOSR Program Officer currently assigned to the award**

Michael R. Berman

**Reporting Period Start Date**

09/01/2015

**Reporting Period End Date**

08/31/2016

**Abstract**

Plasmonic noble metal nanocrystals (NCs) have received a large amount of research interest due to their ability to harvest light and direct it into a small region of space. However, the intrinsic high free carrier concentration of noble metal NCs makes it challenging to achieve plasmonic structures with strong absorption profiles in the near-infrared spectral range, which is relevant for telecommunications and photonics applications. As an alternative to noble metal structures, transition metal oxide NCs possess low intrinsic free carrier concentrations, but can be sufficiently doped such that they display broad plasmon resonances in the near- and mid-infrared spectral regions. Moreover, the free carrier concentrations of metal oxide NCs can be dynamically modified via electrical, chemical, or photonic means, making these promising materials for the design of smart windows with electrically tunable transmission properties and fast photonic gates and switches. However, developing applications based on plasmonic metal oxide NCs requires understanding how the internal structure of these materials impacts both their steady-state absorption properties and how these properties change when a NC is perturbed from equilibrium. In this report, we have used transient absorption spectroscopy to examine how photoexcitation modifies the optical properties of two metal oxide systems, Sn-doped indium oxide (ITO) NCs and oxygen-vacancy

doped tungsten oxide (WO3-x) NCs. Plasmonic excitation of either material generates hot electrons on a sub-picosecond timescale that later cool by releasing their energy to lattice phonons. Both of these processes alter the center frequency and linewidth of a NC's plasmon resonance, but the magnitude of these changes depend on the NC's size, crystallographic structure, and the spatial location of dopants within it. We have also investigated how bandgap photoexcitation can be used to manipulate the plasmon resonance of WO3-x NCs. Adding additional charge carriers into the conduction band of these NCs induces a hypsochromic shift of their plasmon resonance that dissipates on picosecond timescales once the exciting field is removed, making these materials interesting candidates for fast photoswitches and photonic gates.

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